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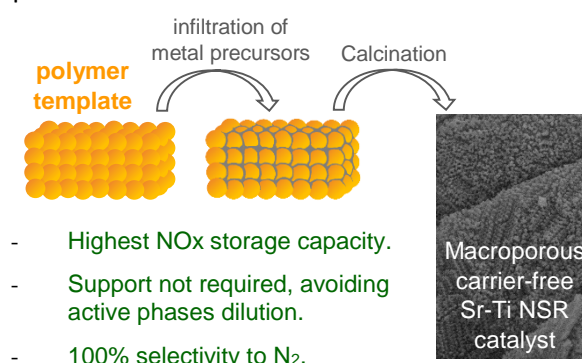
Macroporous Carrier-Free Sr-Ti Catalyst For NO_x Storage and Reduction.

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* Corresponding author: E-mail: agus@ua.es; Tel. (+34) 965903538; Fax. (+34) 965903454. Graphical abstract



Highlights

- A novel Cu-containing Sr-Ti NSR macroporous catalyst has been synthesized
- Its maximum NO_x storage capacity surpasses that of conventional Pt/Ba/Al₂O₃ catalysts
- High NO_x storage is achieved because the active phases are not diluted in an inert carrier
- The macroporous structure is obtained using a colloidal crystal template
- This novel catalyst is totally selective towards N₂ formation as NO_x reduction product

ABSTRACT

A novel concept is presented, consisting of a macroporous carrier-free catalyst. As a proof of concept, a novel Cu-containing Sr-Ti NSR catalyst with a macroporous network has been synthesized, and its maximum NO_x storage capacity (1500 μmolNO_x/g_{catalyst}) significantly surpasses that of conventional Pt/Ba/Al₂O₃ formulations (~600-800 μmolNO_x/g_{catalyst}). This high NO_x storage capacity is achieved because the active phases (mainly SrCO₃ and Cu-containing Sr-Ti perovskites, as deduced by XRD) are not diluted in an inert carrier, and this can be done because the macroporous structure obtained using a polymethylmethacrylate colloidal crystal template allows the access of gases to the particles bulk. *In situ* DRIFTS experiments showed that NO_x were chemisorbed on the novel Cu-containing Sr-Ti macroporous catalyst as a mixture of nitrite and nitro species, and this suggests that several NO_x chemisorption pathways are simultaneously

taking place probably involving chemisorption of both NO and NO₂. Additionally, this novel catalyst is totally selective towards N₂ formation as NO_x reduction product, without traces of N₂O nor NH₃. CO₂ and H₂O compete with NO_x for being chemisorbed on the catalyst, and this hinders the utilization of this catalyst in real diesel exhausts. However, we believe that this new concept of macroporous carrier-free catalyst could be extended to other heterogeneous catalyzed reactions or materials to avoid the diluting effect of the catalyst support.

KEYWORDS. NO_x; NSR; LNT; deNO_x; macroporous; Sr-Ti; mixed oxide; perovskite.

1.- Introduction

Heterogeneous catalytic reactions are an important and complex class of chemical reactions where, usually, reactants and products are gases or liquids and the reaction takes place on the surface of a solid catalyst [1-2]. In these systems, the amount of active sites on the catalyst surface where the fluid molecules are chemisorbed and transformed plays a key role. In order to maximize the amount of active sites exposed to the fluid, the active phases of heterogeneous catalysts are often dispersed on a high-surface area solid carrier. This allows stabilizing small particles of the active compounds, improving their surface/bulk ratio. However, this presents the drawback that the active phases are diluted, and it would be desirable to design catalysts with appropriate solid state, surface, and morphological properties but avoiding the diluting effect of the support.

A particular application where dilution of the active phases presents great disadvantages is NO_x storage and reduction (NSR). NSR is one of the most suitable technologies for NO_x removal in diesel exhausts, which is a hot topic of ongoing research [3-6]. It operates in cycles where NO_x are continuously chemisorbed on a catalyst that is periodically regenerated by feeding pulses of a reductant. Conventional NSR catalysts, like Pt/Ba/Al₂O₃ formulations, combine a NO_x storage compound (typically an alkali compound) with a noble metal to accelerate NO oxidation to NO₂. In this application, high NO_x storage capacity is required, and dispersion and dilution of the active phases has a negative impact in NO_x chemisorption.

To avoid dispersion of the active phases, a novel concept is introduced in this paper. It comprises the preparation of macroporous carrier-free NSR catalysts by using a colloidal crystal template, which allows the access of gases to the particles' bulk. The utilization of colloidal crystal templates has demonstrated to be a suitable synthetic route to obtain solid catalysts with a macroporous structure [7,8], therefore improving the diffusion of gases in heterogeneous catalytic reactions [9-15]. However, macroporous

catalysts prepared with colloidal crystal templates have never been tested for NO_x storage and reduction.

The catalyst prepared in this study is a copper-containing Sr-Ti mixed oxide, mainly consisting of an intimate mixture of SrCO₃ and Sr-Ti perovskites. This mixture of phases has been specially designed to combine the high NO_x chemisorption capacity of the former phase with the NO oxidation capacity of the latter [16-17]. The design and synthesis of specific tailor-made mixed oxides able to perform complex functions is one of the main topics of research in the field of heterogeneous catalysis, and strontium titanates are mixed oxides with relevant catalytic applications [18-23]. The storage and reduction of NO_x has been reported on copper-containing SrTiO₃ [20], this catalyst being also active to accelerate diesel soot combustion [21]. Doped strontium titanates have been also proposed as potential materials for anodes in solid-oxide fuel cell operating directly on hydrocarbon fuels, because of the resistance towards carbon formation [24], for photocatalytic production of H₂ [25], and for propane [26] and methane [27] oxidation.

The goal of this study is to demonstrate the high NO_x storage capacity of the macroporous carrier-free catalyst prepared, and that stored NO_x can be properly reduced to N₂.

2.- Experimental details

2.1. Catalysts preparation.

As a proof of concept, three catalysts have been prepared and tested, which are referred to as SrTi-macro, SrTiCu-macro and SrTi-ref. The catalysts SrTi-macro and SrTi-ref have the same composition, but the former has been prepared by infiltration of the metal precursors in a polymethylmethacrylate (PMMA) colloidal crystal template, which is removed by calcination, while the latter has been obtained by calcination of a

mixture of precursors. The catalyst SrTiCu-macro is similar to SrTi-macro but doped with copper.

Polymethylmethacrylate (PMMA) colloidal crystals were prepared by polymerisation in boiling aqueous solution of methylmethacrylate, methacrylic acid and divinylbenzene in 100:1:5 volume ratio. Potassium persulfate was used to initiate the polymerization, which was conducted for 75 minutes. After cooling, the colloidal crystals of PMMA spheres were conformed by centrifugation.

For preparation of SrTi-macro, 5 g of PMMA template was impregnated with a 1:1 water:etanol solution of strontium nitrate (1.15 grams of strontium nitrate per gram of PMMA). After drying, titanium tetraisopropoxide (0.48 g per gram of PMMA) diluted in 2-propanol was impregnated and the solid was dried at 80 °C. The Sr:Ti atomic ratio used was 3.2, that is, there is an excess of Sr with respect to that required to yield the SrTiO₃ perovskite. The goal was to prepare a mixture of phases combining SrCO₃ (with high NO_x storage capacity) and SrTiO₃ (with high NO oxidation capacity). This was confirmed by XRD and microFRX (see below). The catalyst referred to as SrTiCu-macro was prepared following the same procedure, but in this case, copper nitrate was impregnated into PMMA together with strontium nitrate (strontium nitrate:copper nitrate weight ratio 34.5). The impregnated PMMAs were calcined at 650 °C for 1 hour (heating rate of 1 °C/min) and the temperature was increased afterwards at 10 °C/min up to 850 °C. The reference catalyst, (SrTi-ref) was prepared with the same composition than SrTi-macro but without PMMA template.

For comparison, a reference 1%Pt/10%Ba/Al₂O₃ catalyst was also prepared. Ba(CH₃COO)₂ was loaded on commercial γ -alumina (Alfa Aesar 99.97%) by wetness impregnation using a water solution to reach 10 wt.% Ba, and after drying at 80 °C overnight, the same procedure was repeated with Pt(NH₃)₄(NO₃) for 1 wt. % Pt loading. Finally, the catalyst was dried at 100 °C for 4 hours and calcined at 550 °C for 4 additional hours.

2.2. Catalysts characterization.

SEM images were obtained in a JEOL microscope, model JSM-840.

The porous structure of the catalysts was studied by mercury intrusion porosimetry and N₂ adsorption-desorption at -196 °C. N₂ adsorption-desorption isotherms were obtained in an automatic volumetric system (Autosorb-6, Quantachrome) and data were evaluated by calculating BET surface areas. The catalysts were outgassed at 150 °C for 4 hours before the N₂ adsorption measurements.

Mercury porosimetry analysis was performed in a Poremaster 60 GT (Quantachrome). This equipment is capable of intruding mercury up to 60000 psi reaching pores with diameters of 3.6 nm. All powdered samples were submitted to a prior outgassing treatment at 50 °C under vacuum (10 Torr) for 12 hours. Samples were then analyzed in low pressure mode and high pressure mode consecutively. A contact angle (θ) of 140 °C and a value of mercury surface tension (γ) of 0.48 J/m² were used. Intrusion pressure relates inversely to the pore diameter through the Washburn equation but has to be reminded that pore diameter obtained relates to the entrance of the pore while pore diameter through the channel may vary [28]. Mercury porosimetry of powder samples is complex due to the occurrence of interparticle and intraparticle intrusions as well as bed packing effects. Such effects are considered to occur up to a pressure of 50 psia, which corresponds to a pore diameter of 2133 nm. For the sake of clarity, interparticle filling region is not shown (diameter greater than 2100 nm). Also, intrusion in pores smaller than 10 nm is not shown, as most probably is affected by compressibility of the sample.

The nature of the different crystallographic phases present on the catalysts was studied by XRD, and the composition by Micro-FRX. Diffractograms were obtained in a Rigaku Miniflex II diffractometer, using CuK α radiation (λ = 0.15418 nm), between 10 and 60° (2 θ) with a step of 0.025°. Micro-XRF measurements were performed in an Orbis Micro-XRF Analyzer from EDAX. Areas of 300 μ m in diameter were analyzed and three

different spots were measured and averaged to obtain the mean composition of each catalyst.

The reducibility of the catalysts was studied by H₂-TPR experiments, which were performed in a Micromeritics Pulse ChemiSorb 2705 device. 40 mg of catalyst were loaded on a tubular quartz reactor with 5 mm inner diameter coupled to a thermal conductivity detector. The heating rate was 10 °C/min from room temperature to 1000 °C and the gas flow was 40 ml/min with 5 vol. % H₂ in Ar. A cold trap was placed before the TCD, consisting of a mixture of isopropyl alcohol and liquid nitrogen (temperature - 89 °C).

2.3. NO_x chemisorption and NSR experiments.

NO_x chemisorption-desorption experiments were performed in temperature ramp conditions in a fixed-bed reactor coupled to specific NDIR-UV gas analyzers for NO, NO₂ and O₂ monitoring (Fisher–Rosemount, models BINOS). A gas stream (500 ml/min; GHSV = 30000 h⁻¹) with 500 ppm NO + 5 % O₂ in N₂ was used, and the experiments consisted of heating the reactor from room temperature up to 800 °C at 10 °C/min. The catalysts were kept at room temperature under the reaction gas mixture for 15 minutes before heating, but chemisorption in these conditions was null for all catalysts.

In situ DRIFTS isothermal experiments were performed at 450 °C with catalysts SrTi-macro and SrTiCu-macro, to identify the nature of the chemisorbed NO_x species. An infrared spectrometer Jasco, model FT/IR-4100, was used with a reaction cell that allows temperature and gas flow composition control. The cell was designed to allow the gas flow through the catalytic bed, consisting of 100 mg of undiluted catalyst. The temperature was increased up to 450 °C in inert gas (Ar), and after 30 minutes a background spectrum was recorded and subtracted from further spectra. Then, the inert gas was replaced by 100 ml/min of a gas stream with 500 ppm NO + 5 % O₂ in Ar and the chemisorbed species were monitored as a function of time.

Isothermal NO_x storage and NSR experiments were carried out in a fixed-bed reactor coupled to a mass spectrometer Pfeiffer Vacuum (model OmniStar) running at 1 second frequency. The experiments were performed with 80 mg of the catalyst SrTiCu-macro diluted with 300 mg of SiC. The temperature was increased up to 450 °C in Ar flow, and then the inert gas was replaced by the reaction gas mixture (100 ml). The NO_x chemisorption experiments were carried out with 500 ppm NO + 5% O₂ in Ar. The NSR experiments were also performed with 500 ppm NO + 5% O₂ in Ar and with 500 ppm NO + 5% O₂ + 5 % CO₂ + 5% H₂O in Ar. All gasses were added to the mixture using mass flow controllers except H₂O, than was feed passing the gas mixture through a gas saturator. NSR experiments were carried out with H₂ pulses using an injection valve with a 100 µl loop that was periodically filled with pure H₂ at 10 psi. H₂ was feed to the main stream at 2 minutes intervals.

3.- Results and discussion

3.1 Catalysts Characterization by SEM, mercury porosimetry and N₂ adsorption.

Figure 1 shows images of the PMMA colloidal crystal template (Figure 1a), SrTi-macro catalyst (Figure 1b) and SrTi-ref catalyst (Figure 1c). Monodisperse spheres of PMMA with about 200 nm diameter are observed in Figure 1a, which are packed in regular planes forming the colloidal crystal. The catalyst prepared by infiltration into the PMMA template (Figure 1b) shows the opposite morphology, with large spherical macropores arranged in the same way as the PMMA spheres. On the contrary, the reference catalyst (Figure 1c), prepared without template, shows the agglomeration of large particles.

These important differences in the morphology of the catalysts prepared with and without PMMA template significantly affect the materials macroporosity, and in the end, the catalytic behavior of the solids. Pore size distributions determined by mercury

intrusion porosimetry are included in Figure 2, where the vertical line at a diameter of 50 nm indicates the pore size limit between mesopores and macropores according to the IUPAC recommendation [29]. Mercury intrusion (Figure 2) shows that catalysts termed macro present little porosity in the mesopore range, most of their porosity being in the range of macropores. This confirms that PMMA templating is inducing the generation of macropores in materials SrTi-macro and SrTiCu-macro that are not present in the reference material SrTi-ref.

Figure 3 shows the N₂ adsorption-desorption isotherms at -196 °C of the prepared catalysts. Isotherms are non-reversible Type II isotherms with H3 hysteresis in the range of relative pressures (p/p_0) between 0.8-1 [29]. No presence of pore-blocking artifacts at the end of the hysteresis loop is observed [28]. This fact can be important from the point of view of improving diffusion of gases in the catalytic systems. These features are representative of porous solids with no presence of micropores (< 2nm) or small mesopores (2-10 nm), a low contribution of larger mesopores (10-50 nm) and an important contribution of macropores arranged in some sort of 3D pore network, as indicated by the histeresys loop.

Table 1 presents BET surface areas obtained from N₂ adsorption isotherms at -196 °C and also mercury intrusion porosimetry areas. All surface areas are very low, which is consistent with the absence of micropores and small mesopores on the samples. PMMA-templated samples present slightly higher BET and Hg porosimetry areas than the non-templated sample, supporting the idea that template is inducing the generation of macroporosity. It is important to note that mercury intrusion porosimetry areas are expected to be slightly overestimated in some cases due to overlapping compressibility effects that are difficult to separate from pore intrusion phenomena.

3.2. Catalysts characterization by XRD and MicroFRX

Diffraction patterns of the catalysts are included in Figure 4 and results of the MicroFRX analysis on Table 2, where it is observed that Sr is the most abundant metal on all catalysts.

All diffraction patterns evidence the presence of several phases, including TiO₂ (rutile), SrCO₃, Sr₂TiO₄ and SrTiO₃, and the main peaks of these phases have been labelled in Figure 4. These species have also been detected by other authors for Sr-Ti mixed oxides calcined at temperatures similar to those used in this study [30]. The SrTiO₃ perovskite phase is formed through the reaction of TiO₂ with SrO, which first yields Sr₂TiO₄ [31], and afterwards, by prolonged annealing in presence of TiO₂, would form the SrTiO₃ perovskite phase. Therefore, Sr₂TiO₄ phase is an intermediate in the formation reaction of SrTiO₃ and this explains its modified-perovskite structure, which can be considered as a stacking of Sr-terminated SrTiO₃ perovskite [001] slabs [32].

The rutile (TiO₂) peak at 27.0° is absent in the copper-free catalysts and is quite small in the copper-containing one. This is consistent with the low amount of Ti with regard Sr detected by MicroFRX (Table 2). CuO peaks are not identified in the diffraction pattern of the catalyst SrTiCu-macro, which means that either copper cations are located in the Sr₂TiO₄ and/or SrTiO₃ perovskite structures, or segregated CuO, if present, is well dispersed and is not detected by XRD.

The crystal sizes of Sr₂TiO₄ and SrCO₃ have been determined with the Scherrer equation and the results, which are included in Table 2, are quite similar for all catalysts suggesting that there are not important differences among them.

In conclusion, Micro-FRX and XRD characterization point out that, in spite of the complex composition of the catalysts, they mainly consist of SrCO₃ and the Sr-Ti perovskite-like structures Sr₂TiO₄ and/or the SrTiO₃. This combination of phases is very favorable for NO_x removal by NSR technology, because it combines SrCO₃, which has

high NO_x storage capacity, with copper-containing Sr-Ti perovskites, which accelerate NO oxidation to NO₂, both being intimately mixed.

3.3. Catalysts characterization by Temperature Programmed Reduction with H₂ (H₂-TPR).

The reduction profiles obtained in H₂-TPR experiments are included in Figure 5, where all catalysts show a high temperature reduction peak around 850 °C that must be attributed to bulk reduction of the Sr-Ti mixed oxides. The areas under these peaks evidence that the bulk reduction of catalysts with macroporous structure is improved with regard to that of the reference catalysts prepared without PMMA template. Probably, the macroporous structure improves the diffusion of H₂ into the solid allowing a more efficient reduction.

The copper-containing catalyst (SrTiCu-macro) is more reducible than the copper-free counterpart (SrTi-macro), as expected due to the reduction of copper cations and to the catalytic effect of copper on the reduction of the SrTi perovskite structures. In addition, the copper-containing catalyst shows a lower temperature peak (200-500 °C) that could be tentatively assigned to the reduction of segregated copper oxide, to the reduction of surface Sr-Ti perovskites catalyzed by metal copper and/or to the reduction or release of species like carbonates or hydroxyls.

These H₂-TPR experiments allow concluding that the macroporous structure favors bulk reduction of the mixed oxides with regard to non-macroporous counterparts, and the improved accessibility of gases to the particles bulk would also explain the enhanced chemisorption of NO_x and the extremely high NO_x storage capacity of the SrTiCu-macro catalyst, as shown below.

3.4. NO_x chemisorption

The chemisorption and desorption of NO_x on the catalysts was studied by Temperature Programmed Reactions in a fixed-bed reactor. Figure 6a shows the NO_x profiles as a function of temperature and Figure 6b the corresponding NO₂ profiles. All catalysts chemisorb NO_x above 300 °C approximately, and the stored NO_x decompose at higher temperature closing the mass balances. The amount of NO_x chemisorbed and released depends on the catalyst composition and structure. For comparison purposes, the NO_x chemisorption-desorption profile obtained with the catalyst referred to as SrTiCuO₃-Ref [16] has been also included in Figure 6a. This is the best copper-containing strontium titanate we had tested so far for NO_x storage, and details about its preparation (sol-gel method; 850 °C calcination), characterization, NO_x chemisorption and NSR performance were previously reported elsewhere [16,17]. The macroporous copper-containing catalyst (SrTiCu-macro) significantly outperforms its behavior, as deduced from the areas of the chemisorption and desorption peaks. This enhanced chemisorption of NO_x on the macroporous catalyst SrTiCu-macro with respect to SrTiCuO₃-Ref [16] is assigned to a better accessibility of NO_x into the particles' bulk.

On the other hand, the copper-containing catalyst (SrTiCu-macro) chemisorbs more NO_x than the copper-free counterpart (SrTi-macro), as expected. This improved chemisorption upon copper loading can be related to the improved NO oxidation capacity, as it has been previously reported [24]. It is known that copper accelerates the oxidation of NO, and that NO₂ is chemisorbed much better than NO. Nevertheless, Figure 6b does not show higher NO₂ production by the copper containing catalyst, and this is because the NO₂ yielded is not released, but it remains chemisorbed on the catalyst. All NO₂ profiles of Figure 6b are quite similar, increasing above 400 °C approximately and decreasing after the maxima are attained. Note that the release of NO₂ (Figure 6b) starts at temperatures well above the onset of NO_x chemisorption temperature (Figure 6a), and this is consistent with the hypothesis about NO₂ chemisorption. Worth to mention is

the fact that the NO_2 profiles exceed the equilibrium concentration at the maxima, because part of the NO_2 released at the maxima come from the decomposition of the NO_x species stored at lower temperatures, and not only from the catalytic oxidation of NO taking place at that temperature [33].

The maximum NO_x storage capacity of the catalyst SrTiCu -macro catalyst was measured under isothermal conditions at 450 °C, which is the temperature of the maximum in NO_x chemisorption observed in Figure 6. This NO_x storage capacity is included in Table 3 together with values of reference materials reported in the literature. For each catalyst, and when indicated in the original source, the data included in Table 3 corresponds to the temperature of maximum NO_x storage capacity. NO_x storage capacity was also measured in this study for a reference catalyst with composition 1%Pt/10%Ba/ Al_2O_3 catalyst.

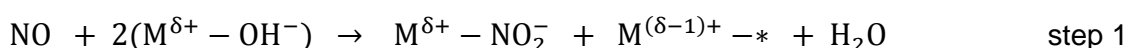
Data on Table 3 show that the NO_x storage capacity of the macroporous carrier-free catalyst SrTiCu -macro prepared with the colloidal crystal template is very high and outperforms the storage capacity of other reported catalysts, including those containing noble metals. It amounts to 1500 $\mu\text{molNO}_x/\text{g}_{\text{catalyst}}$, which is twice, for instance, that stored by a reference 1%Pt-10% Ba/ Al_2O_3 catalyst [34] and also much higher to that chemisorbed by our reference 1%Pt/10%Ba/ Al_2O_3 catalyst (271 $\mu\text{molNO}_x/\text{g}_{\text{catalyst}}$) measured in this study in the same experimental set up than SrTiCu -macro.

This high NO_x storage capacity of SrTiCu -macro can be explained considering that the active species for NO oxidation and NO_x storage are not dispersed (and diluted) on Al_2O_3 , as it must be done with conventional barium-based catalysts to obtain good dispersion. In our case, the macroporous structure allows utilization of the active species of the catalyst (mainly copper-containing strontium titanates and strontium carbonate, as shown in the XRD analysis) without dilution in an inert carrier.

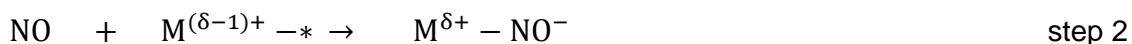
The nature of the chemisorbed NO_x species formed on the catalysts was studied by in situ DRIFTS experiments, and time-resolved spectra obtained with SrTi -macro and

SrTiCu-macro under 500 ppm NO + 5% O₂ gas flow are included in Figure 7a and 7b, respectively.

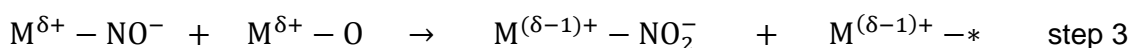
The most relevant peaks of the chemisorbed NO_x species appear in the 1700-1000 cm⁻¹ range. The copper-free catalyst (Figure 7a) shows a single peak at 1260 cm⁻¹ that grows with time and that can be assigned to the formation of chemisorbed nitrites, probably in bridge configuration [35]. On the contrary, the copper-containing catalyst (Figure 7b) shows two peaks, the one assigned to nitrites at 1260 cm⁻¹ and another one at 1355 cm⁻¹ that can be related to the formation of nitro groups [35]. The difference between nitrite and nitro groups is that, in the former, nitrogen oxide is attached to the solid surface by an oxygen atom while in the latter is attached by the nitrogen atom. Adsorbed nitrite/nitro species can be formed upon NO chemisorption on hydroxyl groups [35]:



where “M^{δ+} – OH[–]” are hydroxyl groups attached to metal cations that can accomplish the redox cycle M^{δ+}/M^{(δ–1)+}, that is, Ti and/or Cu cations in our catalysts. The chemisorption of NO on such hydroxyls yields an adsorbed nitrite/nitro “M^{δ+} – NO₂[–]” and leaves an oxygen vacancy “M^{(δ–1)+} – * ” on the catalysts that must be filled in a further step with oxygen from molecular oxygen or with NO, yielding nitrosyl anions “M^{δ+} – NO[–]” as follows



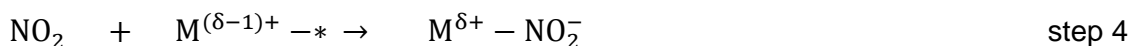
Nitrosyl anions are hardly identified by infrared spectroscopy because their bands overlap with those of nitrites but, in oxidizing conditions, can be formed as transient species in the formation of nitrites/nitro:



The formation of nitrites/nitro throughout step 2 + step 3 requires the participation of easily reducible cations that must be able to provide oxygen for nitrosyl oxidation (step

3). This mechanism is expected to be enhanced by the presence of copper, since cations of this element accomplish redox cycles much more easily than those of Ti.

An additional reaction pathway for nitrite/nitro formation would involve the catalytic oxidation of NO to NO₂, and the chemisorption of NO₂ on partially reduced cations (step 4):



The mechanism involving step 4 is also more probable to occur on the copper-containing catalyst (SrTiCu-macro) than on the copper-free one (SrTi-macro), because copper improves the oxidation capacity of the catalyst and this is necessary for NO₂ production [36].

The simultaneous formation of nitrite and nitro groups on the SrTiCu-macro catalyst (Figure 7b) suggests NO_x chemisorption by different mechanisms and/or the presence of chemisorption sites of different nature, while the only formation of nitrites on SrTi-macro catalyst (Figure 7b) indicates that the NO_x chemisorption mechanism is simpler in this case. One hypothesis could be that NO chemisorption on the copper-free catalyst (SrTi-macro) only involves step 1 while NO_x chemisorption on SrTiCu-macro additionally involves steps 2 to 4 together with step 1.

As a summary of the NO_x chemisorption experiments and of the DRIFTS experiments, it is concluded that the SrTi catalysts chemisorb NO_x above 300 °C approximately. Copper improves the NO_x chemisorption capacity of the Sr-Ti catalyst and modifies the NO_x chemisorption mechanism, involving several simultaneous chemisorption pathways and/or creating chemisorption sites of different nature. The macroporous structure of the catalyst drastically improves the NO_x chemisorption capacity with regard to conventional-shaped catalysts.

3.5. NSR experiments.

NSR experiments were carried out at 450 °C with SrTiCu-macro, and the NO_x profile is shown in Figure 8a. During the NSR cycles performed with NO_x + O₂ in Ar, the chemisorption of NO_x on the catalyst decreased NO_x concentration from 500 ppm in the inlet gas to 200 ppm, keeping the removal of NO_x constant for consecutive NSR cycles. This evidences an appropriate balance between the amounts of NO_x chemisorbed and reduced, and confirms that SrTiCu-macro behaves properly as NSR catalyst under these experimental conditions. After 30 minutes, CO₂ and H₂O was included in the gas mixture and NO_x concentration increased drastically, even above the concentration in the inlet gas. This indicates that the NO_x species chemisorbed on the catalyst in the absence of CO₂ and H₂O get unstable and are released in the presence of these species. This is attributed to the competition of CO₂, H₂O and NO_x for the chemisorption sites of the catalyst. Note that the concentrations of CO₂ and H₂O in the inlet gas (5 %) are much higher to that of NO_x (500 ppm). This is confirmed in Figure 8b, where the CO₂ profile (m/z 44) is shown. It is observed that the m/z 44 signal does not increase rapidly once CO₂ is included in the reaction gas mixture, but raises smoothly because CO₂ is being chemisorbed on the catalyst. The same behavior is expected for H₂O, but in this case was not possible to follow the H₂O profile because a cold trap at – 89 °C was located after the reactor to protect the mass spectrometer from the high H₂O concentration.

Finally, the products selectivity was analyzed for NSR experiments performed under NO_x + O₂ in Ar, and a representative NSR cycle is shown in Figure 9, including the profiles of the potential NO_x reduction products (m/z 28 (N₂), m/z 44 (N₂O) and m/z 17 (NH₃)). Only a N₂ peak is observed, and this is the desired product while N₂O or NH₃ undesired byproducts. These results confirm the high selectivity of the catalyst SrTiCu-macro towards the desired reduction product and the absence of byproducts.

In conclusion, these experiments evidence that the catalyst SrTiCu-macro behaves properly as NSR catalyst in the absence of CO₂ and H₂O, but not in the

presence of these gases. This is a problem for the utilization of this catalyst in a real diesel exhaust. However, although only a NSR catalyst has been tested as a case study, we believe that the concept of carrier-free macroporous catalyst can be extended to other heterogeneous catalytic reactions and also to other materials.

4.- Conclusions.

In summary, it has been demonstrated that the synthesis of macroporous carrier-free catalysts is a successful way to obtain catalysts with very high NO_x storage capacity. As a proof of concept, a macroporous carrier-free copper-containing Sr-Ti catalyst has been prepared with a colloidal crystal template (SrTiCu-macro). This catalyst is able to chemisorb NO_x amounts even higher than those attained by noble metal catalysts. NO_x are chemisorbed on SrTiCu-macro as a mixture of nitrite and nitro species, and this suggests that several NO_x chemisorption pathways are simultaneously taking place probably involving chemisorption of both NO and NO₂, and/or that the catalyst has chemisorption sites of different nature.

The stored NO_x are conveniently reduced by H₂ with total selectivity towards N₂ formation.

CO₂ and H₂O compete with NO_x for the chemisorption sites on the SrTiCu-macro catalyst, and this is a limitation for the utilization of this material as NSR catalyst under real conditions of diesel engine exhaust.

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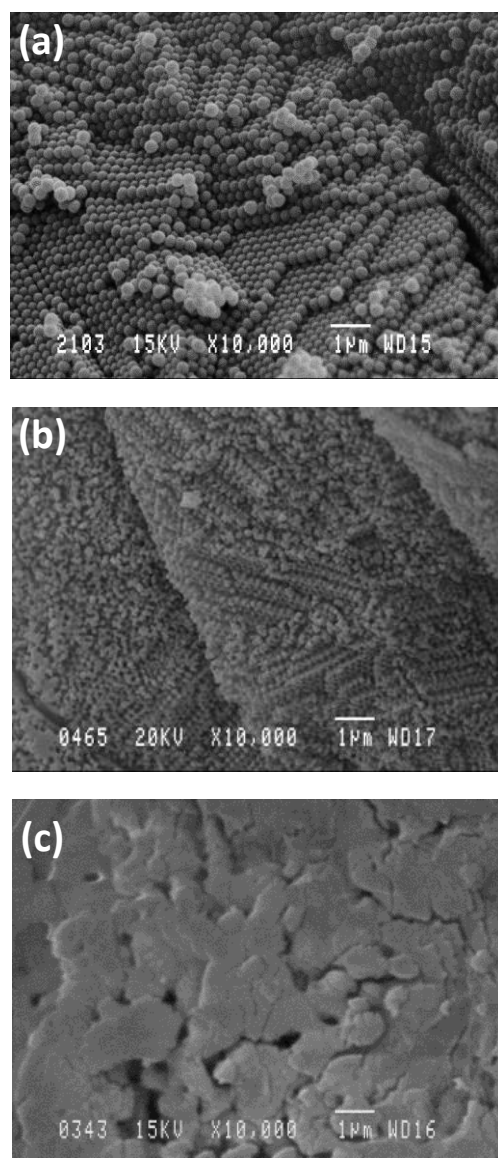


Figure 1. SEM images of (a) PMMA template, (b) SrTi-macro and (c) SrTi-ref.

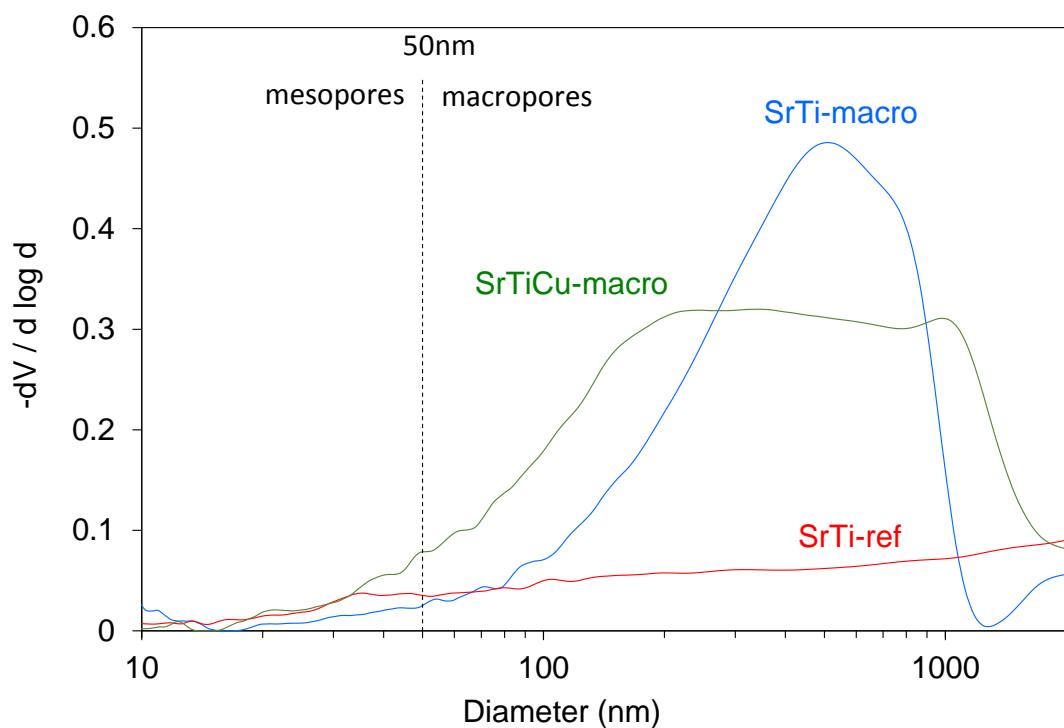


Figure 2. Pore size distribution determined by mercury intrusion porosimetry.

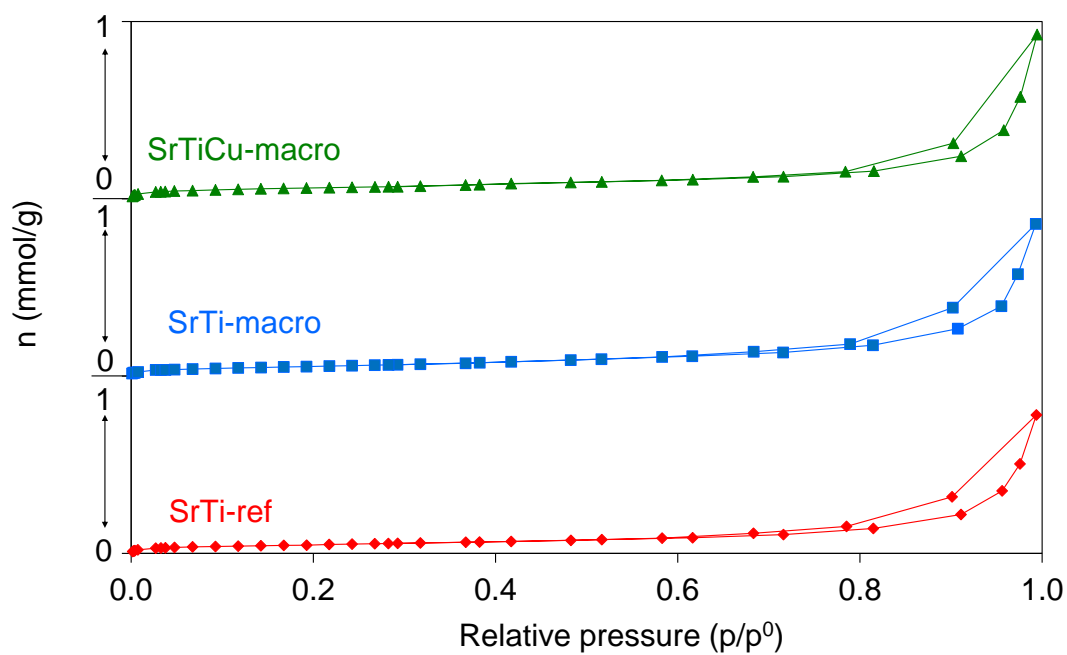


Figure 3. N₂ adsorption-desorption isotherms at -196 °C of the catalysts.

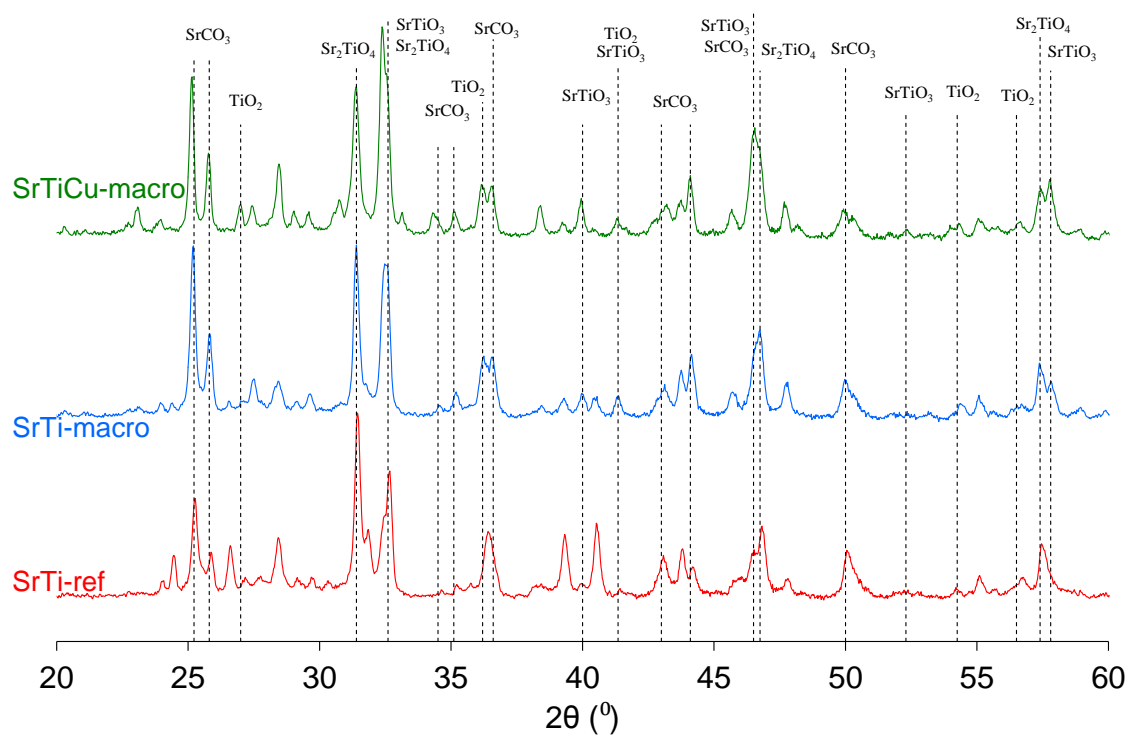


Figure 4. X-Ray diffractograms of the catalysts.

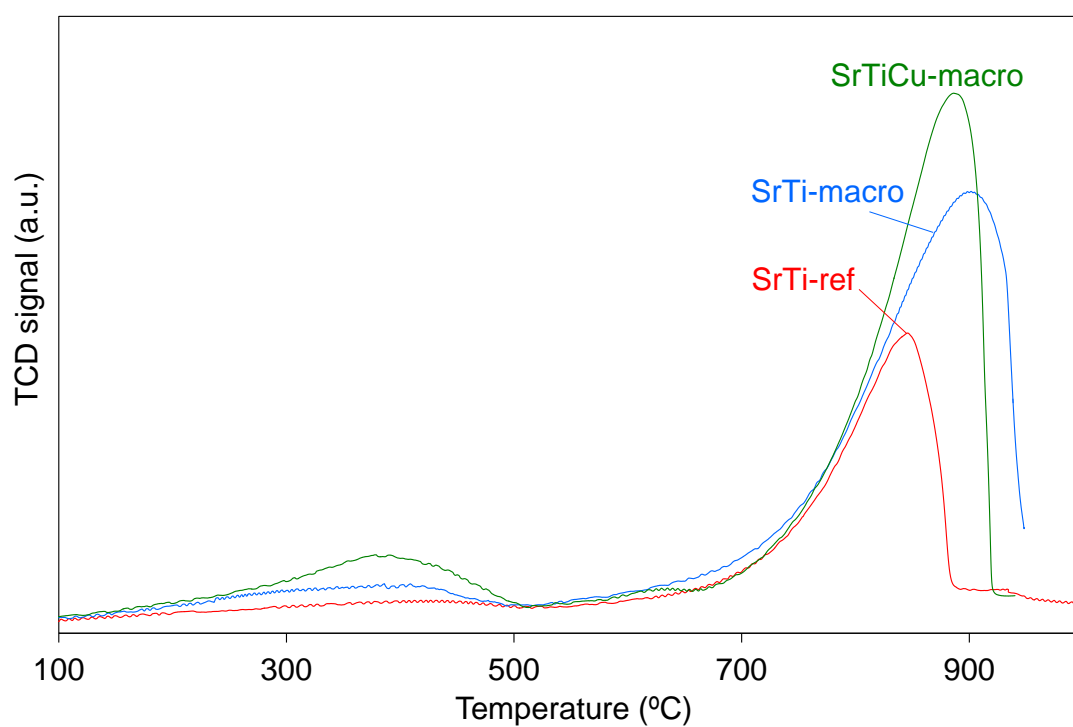


Figure 5. Temperature programmed reductions with H₂.

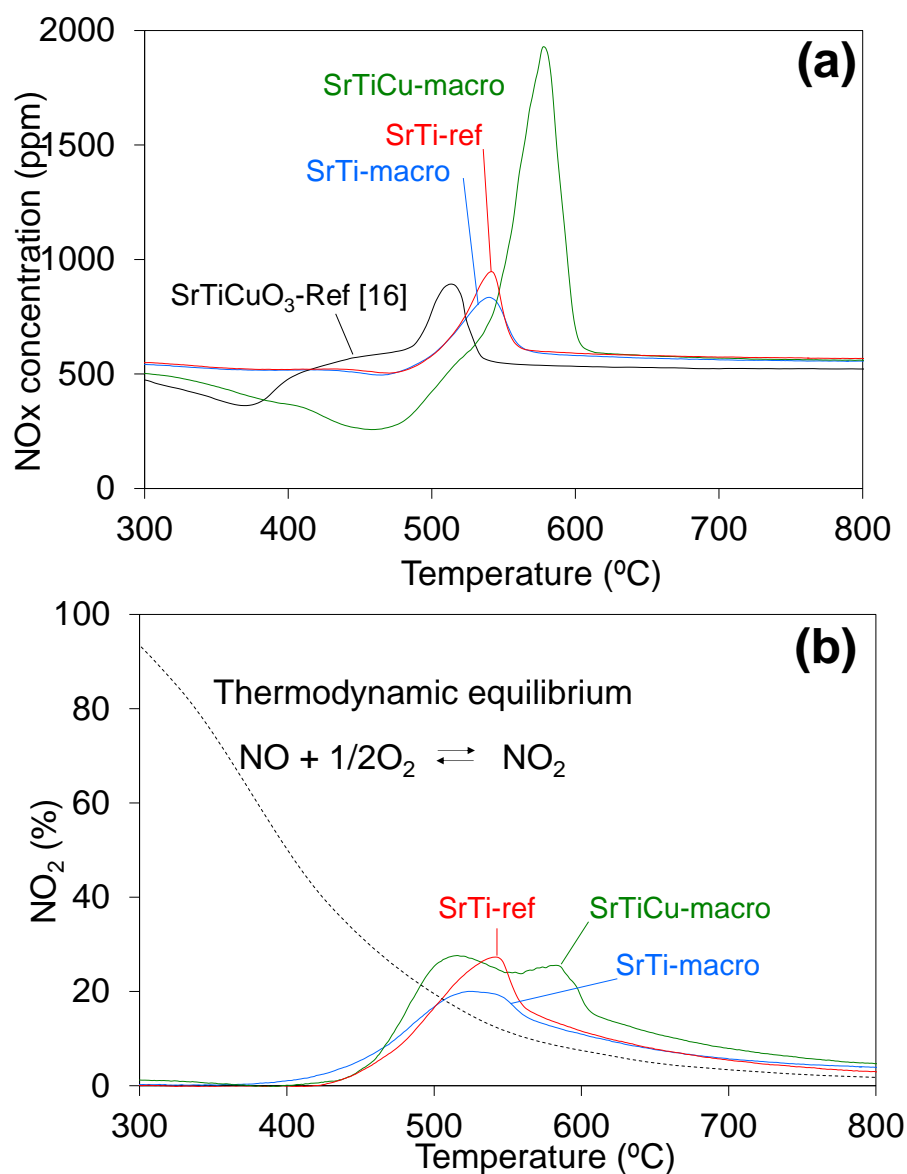


Figure 6. Temperature programmed reactions performed in a gas mixture with 500 ppm NO_x + 5% O₂. (a) NO_x profiles and (b) NO₂ percentages. The catalyst referred to as SrTiCuO₃-Ref [16], which is the best strontium titanate we have tested so far for NO_x storage [16] has been included together with those prepared in the current study for comparison.

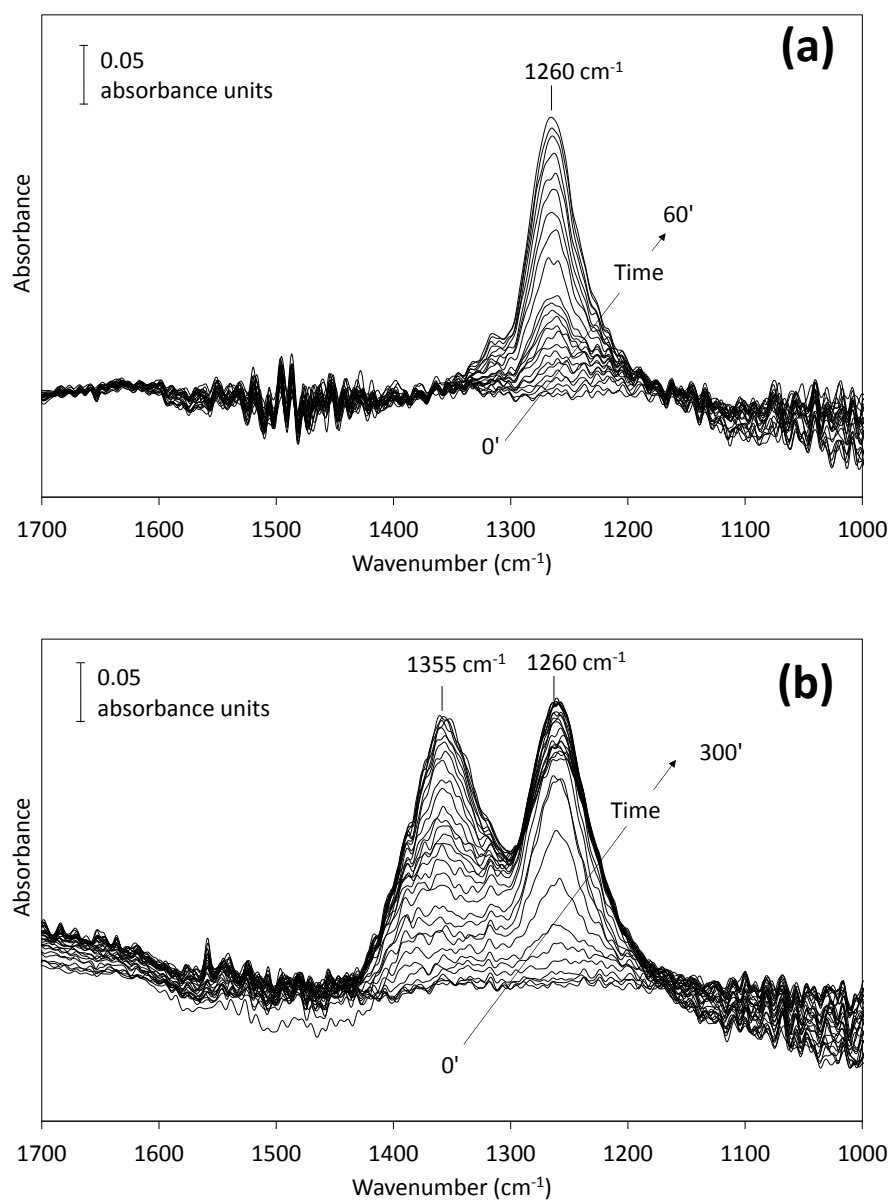


Figure 7. *In situ* DRIFT spectra recorded at 450 °C under 500 ppm NO_x + 5% O₂ stream in the 1700-1000 cm⁻¹ range for nitrogen surface species monitoring. (a) SrTi-macro catalyst and (b) SrTiCu-macro catalyst.

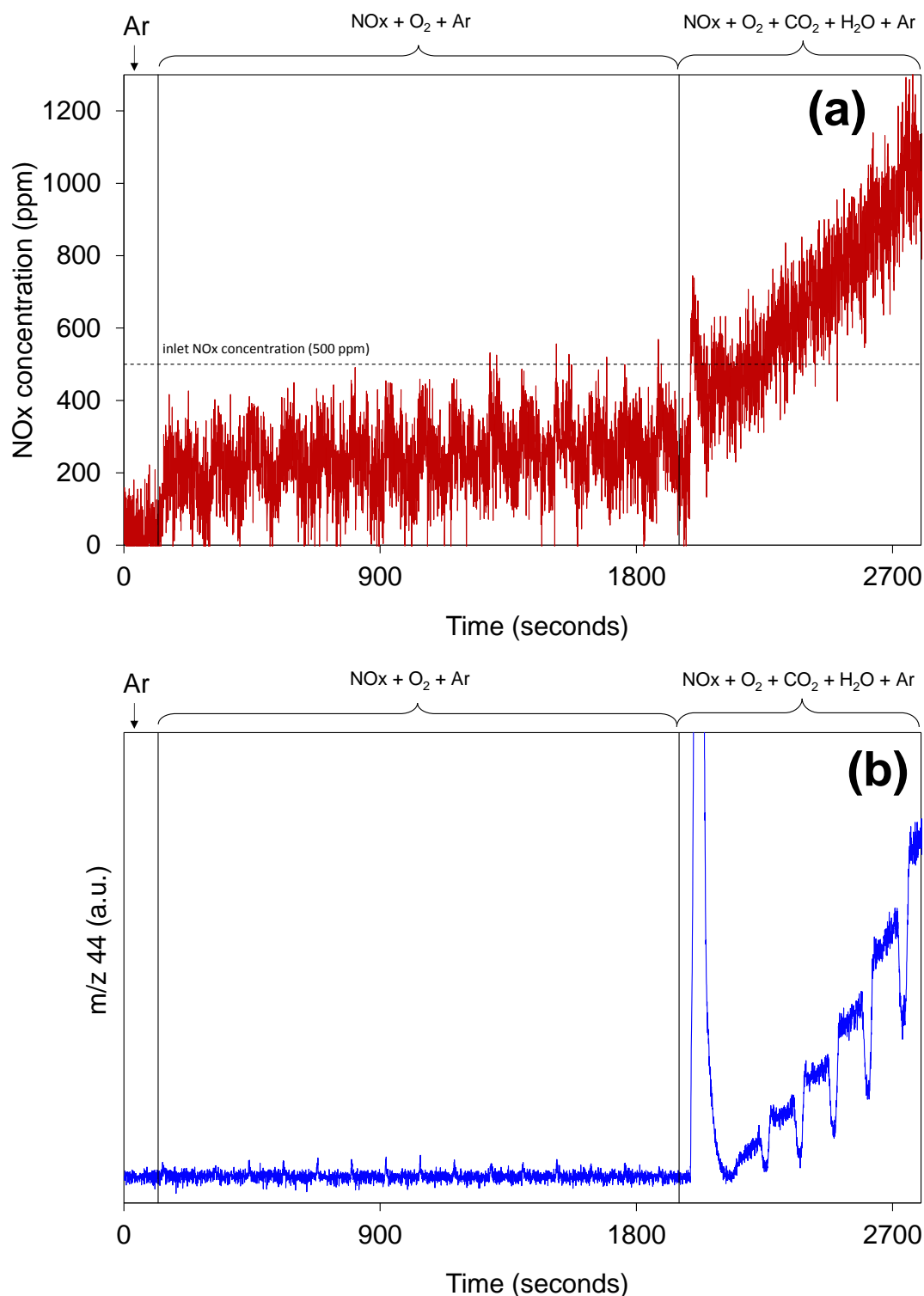


Figure 8. NSR experiments performed with the catalyst SrTiCu-macro at 450 °C under 500 ppm NO + 5% O₂ in the absence and presence of 5 % CO₂ and 5% H₂O and with H₂ pulses. (a) NO_x concentration and (b) m/z 44 signal (corresponding to CO₂ and/or N₂O).

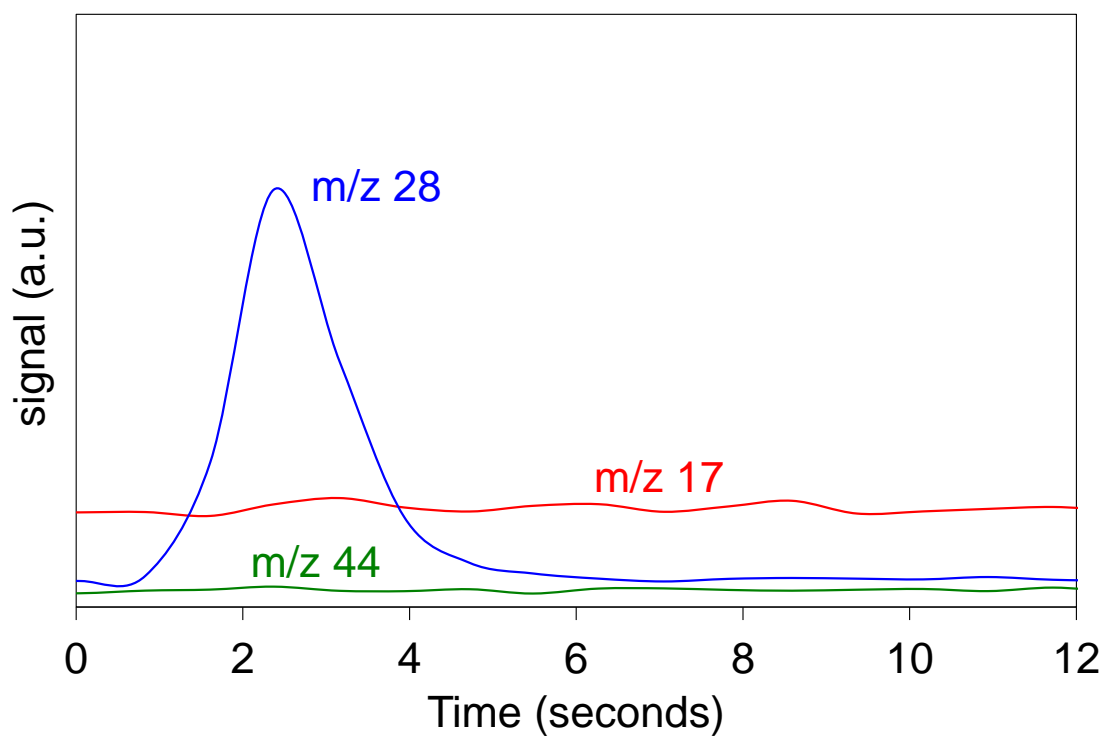


Figure 9. Detail of the NO_x reduction products (m/z 28 N₂, m/z 44 N₂O and m/z 17 NH₃) during a selected H₂ pulse performed in NSR cycles with the catalyst SrTiCu-macro at 450 °C under 500 ppm NO_x + 5% O₂ in Ar.

Table 1. BET specific surface areas and corrected Hg porosimetry surface areas.

Catalyst	BET Surface area (m ² /g)	Hg Surface area* (m ² /g)
SrTiCu-macro	5	6
SrTi-macro	5	5
SrTi-ref	4	4

*Hg porosimetry areas have been corrected ruling out the effect of interparticle intrusion and compressibility effects.

Table 2. MicroFRX characterization of the catalysts and crystal sizes determined with the Scherrer equation.

	Ti (at. %)	Cu (at. %)	Sr (at. %)	SrCO ₃ (nm) peak at 25.2 °	Sr ₂ TiO ₄ (nm) peak at 31.4 °
SrTiCu-macro	15.44 ± 1.45	2.01 ± 0.02	82.55 ± 1.46	43	29
SrTi-macro	13.22 ± 1.83	-	86.78 ± 1.83	39	36
SrTi-ref	13.59 ± 1.69	-	86.41 ± 1.69	42	33

Table 3. Amount of NO_x stored on selected catalysts.

Catalyst	NO _x stored (μmolNO _x /g _{catalyst})	Temperature (°C)	Reference
SrTiCu-macro	1500	450	This work
5%Cu/(BaO/BaCO ₃)	1204	400	[37]
0.24%Pt-8%Mn-20%K/Al ₂ O ₃ -CeO ₂	980	400	[38]
0.8%Pt-23%Ba/Al ₂ O ₃	800	350	[39]
1%Pt-10%Ba/Al ₂ O ₃	714	400	[34]
1%Pt-20%Ba/Al ₂ O ₃	581	300	[40]
Pt-Ru/Ba/Al ₂ O ₃ -Ce _{0.33} Zr _{0.67} O ₂	446	300	[41]
1%Pt/10%Ba/Al ₂ O ₃	271	400	This work
SrTi(Cu)O ₃	244	300	[16,17]
5%Cu/CeO ₂	168	400	[38]